CO$_2$ and N$_2$O from water resource recovery facilities: Evaluation of emissions from biological treatment, settling, disinfection, and receiving water body

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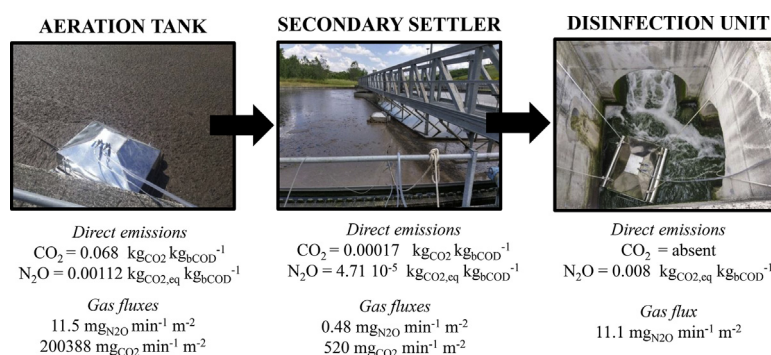[c] Civil & Environmental Engineering Department, University of California, Irvine, CA 92697-2175, USA
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HIGHLIGHTS

- CO$_2$ and N$_2$O emitted during wastewater treatment in water resource recovery facilities
- Floating hood technique utilised for gas collection
- CO$_2$ and N$_2$O emissions from aerated and non-aerated tanks
- Comparison of two methods for the measurement of gas fluxes from non-aerated tanks
- Contribution of disinfection process to N$_2$O emissions from WRRFs

GRAPHICAL ABSTRACT

AERATION TANK

Direct emissions
CO$_2$ = 0.068 kg$_{CO2}$ kg$_{bCOD}^{-1}$
N$_2$O = 0.00112 kg$_{CO2,eq}$ kg$_{bCOD}^{-1}$

Gas fluxes
11.5 mg$_{N2O}$ min^{-1} m^{-2}
200388 mg$_{CO2}$ min^{-1} m^{-2}

SECONDARY SETTLER

Direct emissions
CO$_2$ = 0.00017 kg$_{CO2}$ kg$_{bCOD}^{-1}$
N$_2$O = 4.71 10^{-5} kg$_{CO2,eq}$ kg$_{bCOD}^{-1}$

Gas fluxes
0.48 mg$_{N2O}$ min^{-1} m^{-2}
520 mg$_{CO2}$ min^{-1} m^{-2}

DISINFECTION UNIT

Direct emissions
CO$_2$ = absent
N$_2$O = 0.008 kg$_{CO2,eq}$ kg$_{bCOD}^{-1}$

Gas flux
11.1 mg$_{N2O}$ min^{-1} m^{-2}

ARTICLE INFO

ABSTRACT

Water resource recovery facilities (WRRFs) contribute to climate change and air pollution, as they are anthropogenic potential sources of direct and indirect emission of greenhouse gases (GHGs). Studies concerning the monitoring and accounting for GHG emissions from WRRFs are of increasing interest. In this study, the floating hood technique for gas collection was coupled with the off-gas method to monitor and apportion nitrous oxide (N$_2$O) and carbon dioxide (CO$_2$) emissions from both aerated and non-aerated tanks in a municipal water resource recovery facility, in order to investigate its carbon footprint (CFP). To our knowledge, this is the first time that the chamber technique was applied to evaluate gas fluxes from the settler, where an emission factor (EF) of 4.71 $* 10^{-5}$ kg$_{CO2,eq}$ kg$_{bCOD}^{-1}$ was found. Interesting results were found in the disinfection unit, which was the major contributor to direct N$_2$O emissions (with a specific emission factor of 0.008 kg$_{CO2,eq}$ kg$_{bCOD}^{-1}$), due to the chemical interaction between hydroxylamine and the disinfectant agent (hypochlorite). The specific emission factor of the biological aerated tank was 0.00112 kg$_{CO2,eq}$ kg$_{bCOD}^{-1}$. The average direct CO$_2$ emission was equal to 0.068 kg$_{CO2}$ kg$_{bCOD}^{-1}$ from the activated sludge tank and to 0.00017 kg$_{CO2}$ kg$_{bCOD}^{-1}$ from the secondary clarifier. Therefore, taking into account the contribution of both direct N$_2$O and CO$_2$ emissions, values of 0.069 kg$_{CO2,eq}$ kg$_{bCOD}^{-1}$, 0.008 kg$_{CO2,eq}$ kg$_{bCOD}^{-1}$ and 0.00022 kg$_{CO2,eq}$ kg$_{bCOD}^{-1}$ were found for the net CFP of the aerated compartment, the disinfection unit and the clarifier, respectively.

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The plant energy Footprint (eFP) was also evaluated, confirming that the aeration system is the major contributor to energy consumption, as well as to indirect CO_2 emission, with a specific eFP of 1.49 kWh kg_{bCOD}^{-1}.

1. Introduction

Water resource recovery facilities (WRRFs) are responsible for the emission of greenhouse gases (GHGs), such as nitrous oxide (N_2O), methane (CH_4), and carbon dioxide (CO_2) (Hwang et al., 2016). Indeed, in 2005 the wastewater sector was responsible for over 5% of global non-CO_2 GHG emissions, which are predicted to increase by 27% by 2030 (U.S. Environmental Protection Agency, 2012). Efforts for monitoring and accounting for GHG emissions from WRRFs are of increasing interest (Monteith et al., 2005; Kampschreur et al., 2008; Kampschreur et al., 2008; Law et al., 2012; Daelman et al., 2013; Caniani et al., 2015; Caivano et al., 2016). In detail, the scientific community divides GHGs emission into direct and indirect emissions (Mannina et al., 2016). The direct GHG emissions are related to the CO_2 equivalent ($CO_{2,eq}$) production from biological processes inside the bioreactors, such as aerobic substrate oxidation, biomass decay, and biological nitrogen removal processes (i.e. nitrification, denitrification, and nitrifier denitrification), and the stripping of dissolved gases in dewatering units (Sweetapple et al., 2013). The latter are related to the $CO_{2,eq}$ production from energy consumption for pumping, aeration, heating, and mixing (Shahabadi et al., 2009), as well as from other sources, which are not controlled inside the plant, and contribute to the assessment of the total energy Footprint (eFP) of the monitored plant.

Several methods have been proposed in the scientific literature for monitoring full-scale plants in terms of GHG emissions (Czepiel et al., 1995; Foley et al., 2010; Ahn et al., 2010; Law et al., 2012; Aboobakar et al., 2013; Caniani et al., 2017). The off-gas method is the most useful tool to evaluate direct emissions from aerated tanks, besides the efficiency performance of aeration systems (Leu et al., 2010). It was developed by Redmon et al. (1983) and consists of a gas-phase mass balance between the inlet and the outlet air. CO_2, N_2O, and CH_4 amounts in the off-gas exiting from the liquid surface can be measured by means of a floating hood for collecting and conveying off-gases to an accurate on-line analyser.

The floating hood apparatus was used for the first time in wastewater treatment units by Czepiel et al. (1995), who measured the off-gas flux from both aerated and non-aerated liquid surfaces. An aluminum box was manually positioned on the liquid surface of the reactor in order to minimize the moving of the wastewater. Furthermore, it was equipped with side floats and with an internal blower to ensure that it was floating and that the gas was stripping. Twenty ml nylon syringes were used to collect gas samples. Gas emissions from the sludge storage tank, in particular N_2O flux, were also quantified by using two methods, i.e. the vacuum vial technique and the floating chamber technique. An off-line gas chromatograph (GC), with a 95% argon and 5% methane mixture as carrier gas, equipped with an electron capture detector (ECD), was used to quantify N_2O loads in the collected samples.

Foley et al. (2010) also used a floating hood to collect the off-gas fluxes from the liquid surface of the bioreactor during aeration periods. The gas samples were collected by means of 1 L Tedlar sampling bags and a GC equipped with ECD. A thermal conductivity detector (TCD) and a flame ionization detector (FID) were used to quantify gas concentrations. An on-line Clark-type microsensor quantified dissolved N_2O loads. The floating hood was equipped with a portable probe to measure some wastewater quality parameters, such as temperature, dissolved oxygen, and oxidation-reduction potential.

The Surface Emission Isolation Flux Chamber (SEIFC) was used by Ahn et al. (2010), consisting of an enclosed floating headspace with a circular section of 0.13 m^2. The gas collection and sampling were performed together with the measurement of the mixed liquor parameters, such as dissolved oxygen (DO), temperature (T), Chemical Oxygen Demand (COD), Total Suspended Solids (TSS), and Volatile Suspended Solids (VSS). At the same time, Total Kijeldal Nitrogen (TKN), NH_4, NO_2^-, and NO_3^- loads were measured in the influent, the effluent, and the mixed liquor to verify the spatial variability of the emissions. An on-line infrared analyser was used to quantify N_2O concentrations in the gas phase.

A mobile floating hood was used by Law et al. (2012) to simultaneously measure off-gas emissions from several mixed liquor points and to verify the spatial-temporal load variations. The gas samples were collected from the hood headspace using 20 ml nylon syringes and a GC equipped with an ECD detector was used to determine gas concentrations. The vacuum vial technique was used to analyse via GC the liquid samples. However, the authors also suggested the use of a Clark-type microsensor as on-line measurement method for the liquid phase. A floating hood with a surface area of 0.34 m^2 was used by Aboobakar et al. (2013) for off-gas collection from the surface of the biological reactor. The N_2O concentrations in both gas and liquid phases were determined by means of an infrared analyser and a Clark-type microsensor, respectively. However, the results proposed in literature often referred to activated sludge systems and experimental activities on the sludge treatment line and on the disinfection units are required. This is important as some disinfectant units could be a potential GHG source in WRRFs. To our knowledge, data about GHG emissions from settlers and thickeners are limited, probably because of the increased difficulties in evaluating direct emissions when there is an absence of an induced air stream through the liquid volume (Caivano et al., 2016). Gas samples, in particular, could not be immediately collected due to the insignificant off-gas flow leaving the liquid surface. Moreover, closed chambers placed on the liquid surface of the monitored tanks can alter the natural partial pressure of gases under the hood headspace, consequently modifying the natural equilibrium between the gas and the liquid phase. However, to overcome the problem, Chandran (2011) suggested to introduce air or a carrier gas through the hood headspace at a known flow rate, thus ensuring the mixing of the hood contents. The GHG flows are calculated as the difference between the incoming and the off-gas flow rates, respectively. The problem is that, giving the very low fluxes of GHGs in non-aerated tanks, the differences between the incoming and the off-gas flow rates are usually negligible.

The static chamber technique was used by Uggetti et al. (2012) to determine the temporal variability of the GHG emissions from sludge treatment wetlands. The chamber was equipped with a fan to ensure thorough gas mixing and the gas fluxes are calculated from the linear increase of the gas concentration in the hood headspace within 40 min monitoring period.

However, the major disadvantage of using a fan to ensure mixing and avoid underpressure in the chamber during gas sampling is that it is not possible to control the air flow rate inside the hood headspace. The air conditions could not be real and the effects of the evaporation on gas transfer could not be quantified. More studies are needed in order to simplify and standardize the monitoring techniques and sampling strategies, specifically in non-aerated tanks (Caniani et al., 2017).

Numerous studies are focused on N_2O, particularly because of its significant global warming potential and because its emission factors show a great variability among different WRRFs (Townsend-Small et al., 2011). However, recent studies have demonstrated that fossil carbon contribution to GHG emission can span from negligible to substantial

in different types of industrial WRRFs. Indeed, the petroleum-derived products contribute to the specific CFP as CO_2, along both the water and sludge line in a WRRF (Schneider et al., 2015; Tseng et al., 2016).

Furthermore, even though a broad spectrum of methods for gas sampling and measuring is available in the literature, a standard method, especially for non-aerated tanks and disinfection units, has not yet been proposed, because of the great variability characteristics and design of WRRFs.

In this study, a medium-sized municipal WRRF located in Basilicata (Southern Italy) was investigated to evaluate the global CFP and eFP and to compare different methods for sampling and measuring GHG direct emissions from non-aerated tanks. For the first time, measurements of the GHG emissions from the disinfection unit were also carried out. The activated sludge (AS) basin, the secondary clarifier, and the chlorination unit were monitored by means of the off-gas method. In particular, the obtained results pay attention to the emissions from treatment units usually neglected in the scientific literature as potential GHG sources (i.e. settler and disinfection), as well as to the CO_2 and N_2O fate in the receiving water body. Indeed, the disinfection unit (i.e. chlorination) revealed to be an important contributor to N_2O emissions because of the chemical reaction between the hydroxylamine (NH_2OH) and the disinfectant agent ($NaClO$), whereas the settler could be an important source of GHG due to the presence of anaerobic zones and incomplete or partial biological nitrogen removal (BNR) processes. N_2O emission fractions were estimated as a percentage of the influent load of nitrogen (N). GHG analyses were performed by using an optimized method based on gas chromatography equipped with a barrier ionization discharge detector (GC-BID) for simultaneous determination of N_2O and CO_2 concentrations (Pascale et al., 2017).

2. Materials and methods

2.1. Experimental site

The municipal WRRF under study is located in the city of Potenza (Basilicata) in Southern Italy. The WRRF serves 160,000 population equivalents (with a wastewater flow of approximately 1730 m^3 h^{-1} on the days of testing) and treats organic matter and nitrogen with a Modified Ludzack-Ettinger (MLE) configuration, which consists of a series of anoxic and aerobic reactors.

A grit chamber is the first physical treatment unit in which sand and heavy solids are removed from the influent. The fluctuations in influent-wastewater flow rates are reduced by means of the equalization basin, through which a constant flow is reached. The wastewater directly enters in the biological compartment. Following the anoxic tank, the mixed liquor enters the aeration tank where aerobic conditions are ensured. The biological compartment consists of two lines of three aerated tanks each with a total volume of 6120 m^3 (68 × 18 × 5 m, L × W × H). The cross-section area of one line of the aerated compartment is 2592 m^2. Aeration in the AS tank is provided through submerged aerators, fed by two blowers working at 132 kW for 24 h day^{-1} with a total air flow rate of 12,000 m^3 h^{-1}. The aeration system is equipped with fine-bubble diffusers (ITT-FLYGT), 9″ in diameter, which have an air flow rate of 3.17 Nm^{-3} h^{-1} each.

The secondary clarifier ensures the biomass separation from the treated wastewater by gravity settling. Further removing of suspended solids is achieved by means of ten filter beds composed of granular materials. The treated effluent is directed to the chlorination unit, fed with 27 l h^{-1} of sodium hypochlorite ($NaClO$ 12% w/v) and it is finally released into a small neighboring stream. The sludge treatment step consists of thickening, Anaerobic Digestion (AD), dewatering and landfilling of the obtained biosolids. The off-gas measurements were performed in the month of June 2016, during a monitoring campaign that lasted 4 days, with the main objective to compare procedures for GHG emission evaluation from non-aerated tank and to assess N_2O emissions from the disinfection unit. Furthermore, concentrations of COD, TSS, ammonia nitrogen (NH_4^+), nitrite (NO_2^-), and nitrate (NO_3^-) in daily composite samples of both influent and effluent, both sampled every hour, were performed on the days of testing (Table 1). Indeed, although the process layout and dynamics have a fundamental role in determining the quantity and quality of the produced GHG, the incoming wastewater characteristics are also some of the primary components that determine the quantity and quality of the produced GHG as well.

The concentrations in the flows to the WRRF were very low because of the high daily water supply, as well as the presence of the combined sewer. Moreover, the dilution phenomena were favored during the testing days due to rain.

In order to ensure further consideration of GHG production and emissions, the concentrations of dissolved CO_2 (here named sCO_2), dissolved N_2O (here named sN_2O), and hydroxylamine (NH_2OH) were evaluated along the water-line.

2.2. Off-gas measurements

In this study, the AS tank, the secondary settler, and the chlorination were monitored using the off-gas technique in order to evaluate direct CO_2 and N_2O emissions. The off-gas method is based on a gas-phase mass balance between inlet and outlet air.

The off-gas test campaigns were conducted using a specific apparatus developed by the Civil and Environmental Engineering Department of the University of Basilicata. A stainless steel floating hood (1 × 0.7 × 0.4 m, L × W × H) with a cross sectional area of 0.7 m^2 and a volume of 280 l was used to capture the gas fluxes from the liquid surface of the reactors (Fig. 1a and c). The mobile floating system allows the sinking of the hood in order to ensure no contamination from atmospheric air. The stainless steel hood was anchored to two cylindrical floats with a diameter of 0.10 m each.

Dissolved gases were transported by stripping due to aeration into the hood headspace, which was connected to a flowmeter (Fig. 1b) through a 16 mm diameter hose. Gas flow rates were measured by using a mass flow meter for compressed air (MISDA DN15 – SATEMA S.a.S.). The flow measurement was performed according to the calorimetric principle by detecting the volumetric flow of the normalized fluid regardless of its temperature and pressure. The flow meter was

Table 1
Characteristics of the WRRF influent and effluent, in term of COD (mg l^{-1}), TSS (mg l^{-1}), NH_4^+ (mg l^{-1}), $N-NO_2^-$ (mg l^{-1}) and $N-NO_3^-$ (mg l^{-1}). Each concentration value was averaged of three replicates (independent samples) and the error was within 5%.

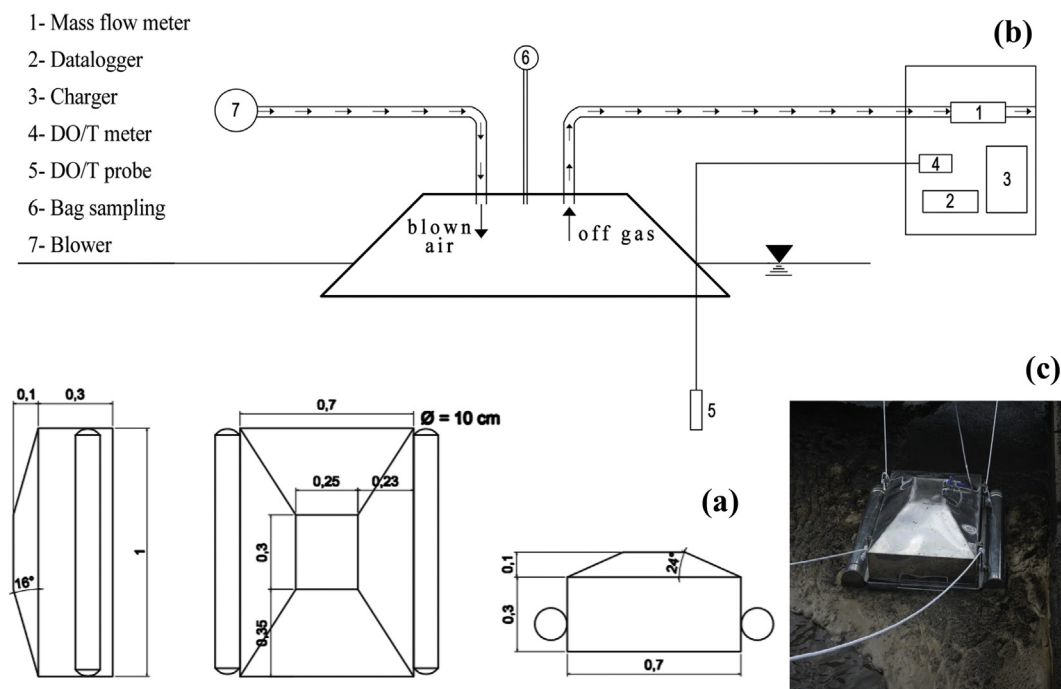|		COD (mg l^{-1})	TSS (mg l^{-1})	NH_4^+ (mg l^{-1})	$N-NO_3^-$ (mg l^{-1})	$N-NO_2^-$ (mg l^{-1})
Influent	June 6th	148	37	9.61	0.13	–
	June 7th	121	29	8.54	0.1	–
	June 8th	129	35	8.62	0.14	–
	June 9th	153	47	11.49	0.08	–
Effluent	June 6th	52	5	0.25	8.34	–
	June 7th	36	7	0.19	7.66	–
	June 8th	45	4	0.31	7.09	–
	June 9th	64	8	0.63	10.7	–

Fig. 1. (a) Floating hood design (the measurements were in meters). (b) Layout of the off-gas apparatus. (c) Picture of the apparatus.

connected to a datalogger to record the off-gas flow rates during the monitoring campaign.

A multi-parameter probe (Rosemount™ RDO Optical Dissolved Oxygen System, Emerson Electric Co., US) for online monitoring of DO and T was positioned close to the off-gas collection hood, 1.5 m deeper from the liquid surface, to ensure operational parameter controls over the liquid volume in the biological tank.

To our knowledge, difficulties in measuring direct GHG emissions increase when there is an absence of an induced air stream through the liquid volume (Caivano et al., 2016). Therefore, an air stream was simulated by using a blower, in order to carry out samplings from the secondary settler. The hood was also equipped with a valve for gas sampling in order to connect suitable sampling bags through a 4 mm diameter hose. The hood was manually positioned and bound with ropes in order to minimize the effect of turbulence, and it was immersed for 10 cm in the liquid to minimize the sample contamination with atmospheric air.

2.3. Sampling procedure in the aeration tank

Gas sampling plans depend on the geometry of the tank and the type of the aeration system. However, the sampling sequence chosen should cover a geometrically representative area of the whole basin of at least 2% of the total tank surface (ASCE, 1997).

One of the three AS tanks was chosen to represent the biological treatment. The hood was positioned in 12 different positions as shown in Fig. 2 to cover 1.95% of the tank surface.

For each sampling point, gas flow measurements were recorded. The 15 minute pre-testing interval was used as it was assumed sufficient for monitoring mass flux, since the aeration through the bulk liquid is continuous (Caivano et al., 2016). The aeration system consists of a submerged fine bubbles diffusers and the aeration rate is fixed.

The flow meter recorded a flow rate value every 30 s for the first 5 min, and then every minute for the last 10 min. Thus, the average flow rates were calculated for each sampling point (Table 2).

A value of 14.27 ($\pm$0.36) Nl min^{-1} was found as an average for the whole tank.

The multi-parameter probe recorded one value of DO and T every 30 s and the average values for DO and T were calculated for each sampling point (Table 3).

Therefore, values of 5.50 ($\pm$0.46) mg l^{-1} and 18.55 ($\pm$0.12) °C were found, respectively, as an average for the whole tank.

DO plays an important role in N_2O production during BNR processes. As we know from the technical literature, when DO in AS is lower than 2 mg l^{-1} (conventional value for a good removal of both BOD and N), the nitrification rate decreases. Therefore, the intermediates, such as N_2O and NH_2OH, could accumulate in the liquid phase.

One liter Tedlar bags (Recom Industriale s.r.l., Italy) were used to collect off-gas samples and carry out off-line measurements of N_2O and CO_2 concentrations. The gas bags were equipped with a vacuum pump and connected to the hood headspace to collect a gas sample from each of the 12 hood positions after 15 min from the starting of flow measurements. The GC was equipped with a BID detector to simultaneously measure CO_2 and N_2O concentrations. The gas samples were filtered through an adsorption column before entering the GC loop, using a PVC column (h = 6 cm, d = 1.5 cm) filled with three gel layers composed of silica-NaOH-silica for moisture and CO_2 removal in order to reduce the CO_2 peak and to make the N_2O peak more visible and evident.

N_2O and CO_2 weighted average concentrations at each sampling point were calculated according to Eqs. (1) and (2) (Gori et al., 2010):

$$\bar{N_2O} = \frac{\sum_{i=1}^{12} N_2O_{,i} \cdot Q_{off-gas,i}}{\sum_{i=1}^{12} Q_{off-gas,i}} \tag{1}$$

$$\bar{CO_2} = \frac{\sum_{i=1}^{12} CO_{2,i} \cdot Q_{off-gas,i}}{\sum_{i=1}^{12} Q_{off-gas,i}} \tag{2}$$

where $N_2O_{,i}$ and $CO_{2,\ i}$ are the gas concentrations in each sampling point and $Q_{off-gas,\ i}$ is the off-gas flow rate in each sampling point.
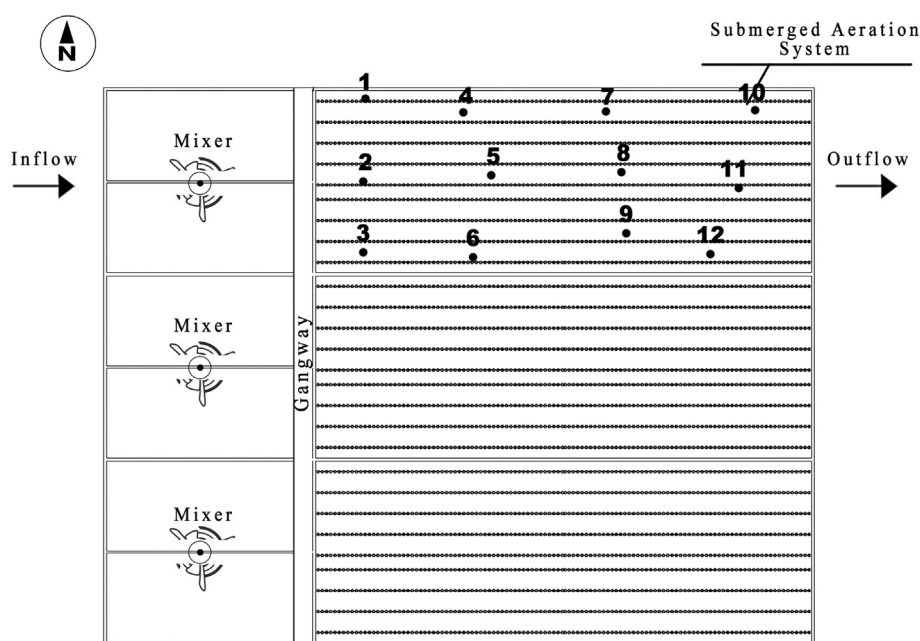
Fig. 2. Layout of the positions of the sampling hood for off gas measurements in one line of the biological aerated unit of the Potenza WWTP.

Table 2
Off-gas flow rates ($Q_{off-gas, i}$) (Nl min^{-1}) during the sampling period.

Sample	1	2	3	4	5	6	7	8	9	10	11	12
$Q_{off-gas, i}$	14.35	14.20	14.43	14.37	13.70	14.01	14.83	14.70	13.92	13.85	14.67	14.23

2.4. Sampling procedure in the secondary settler

Due to the presence of the traveling bridge, a simplified monitoring plan was used in the secondary settler. One of the two working settlers was monitored, choosing one sampling point as representative of the whole tank (Fig. 3a) and assuming that the variation of the emissions on the surface was negligible. The off gas sampling apparatus was fixed to the traveling bridge.

The off-gas hood was set to collect the exhaust gas in the hood headspace, but due to the absence of aeration systems, there was no relevant off-gas flow rate leaving the liquid surface. Furthermore, a change in gas partial pressure should be observed without aeration. Therefore, the floating hood was positioned in one location, fixed to the traveling bridge and connected to a blower using a 10 mm diameter Teflon tube. The blowing air flow rate ($Q_{air,in}$) was set to 1.20 $\cdot$ 10^{-2} Nm^3 min^{-1} to simulate a wind speed of 2.55 $\cdot$ 10^{-3} m s^{-1}, which was actually measured at 40 cm above the water surface level during the testing day. In fact, a well-known air flow rate allowed us to ascribe the emissions to the actual wind speed.

The flow meter recorded a flow rate value every 30 s for 28 min and the average flow rate was 1.23 $\cdot$ 10^{-2} Nm^3 min^{-1} ($Q_{off-gas}$). During the monitoring period, eight off-gas samples were collected at 3, 8, 13, 18, 22, 25, and 28 min (according to Uggetti et al., 2012) after the hood positioning.

Gas fluxes were calculated by means of the increase of the gas concentration in the hood headspace (Uggetti et al., 2012), within the measuring time of 28 min. The increase rate of gas concentration was calculated from the slope of the linear regression for the concentration versus time, as shown in Eq. (3) (Uggetti et al., 2012):

$$Gas\ flux_1 \left[\frac{mg}{min\,m^2}\right] = \frac{slope\left[\frac{mg}{min}\right]}{hood\ cross-sectional\ area\ [m^2]} \cdot hood\ volume\ [l] \qquad (3)$$

The method suggested by Uggetti et al. (2012) was never tested on non-aerated tanks in WWTPs until now.

A second method was applied to evaluate the off-gas flow rate, according to Eq. (4) (Chandran, 2011):

$$Gas\ flux_2 \left[\frac{mg}{min\,m^2}\right] = \frac{\bar{C}_i(Q_{air,in}-Q_{off-gas})\left[\frac{mg}{min}\right]}{hood\ cross-sectional\ area\ [m^2]} \qquad (4)$$

where $\bar{C}_i$ is the weighted average concentration of gases calculated as in Eqs. (1) and (2), $Q_{air, in}$ is the blowing air flow rate, and $\bar{Q}_{off-gas}$ is the off-gas flow rate.

Table 3
Values of DO (mg l^{-1}) and T (°C) in each sampling point.

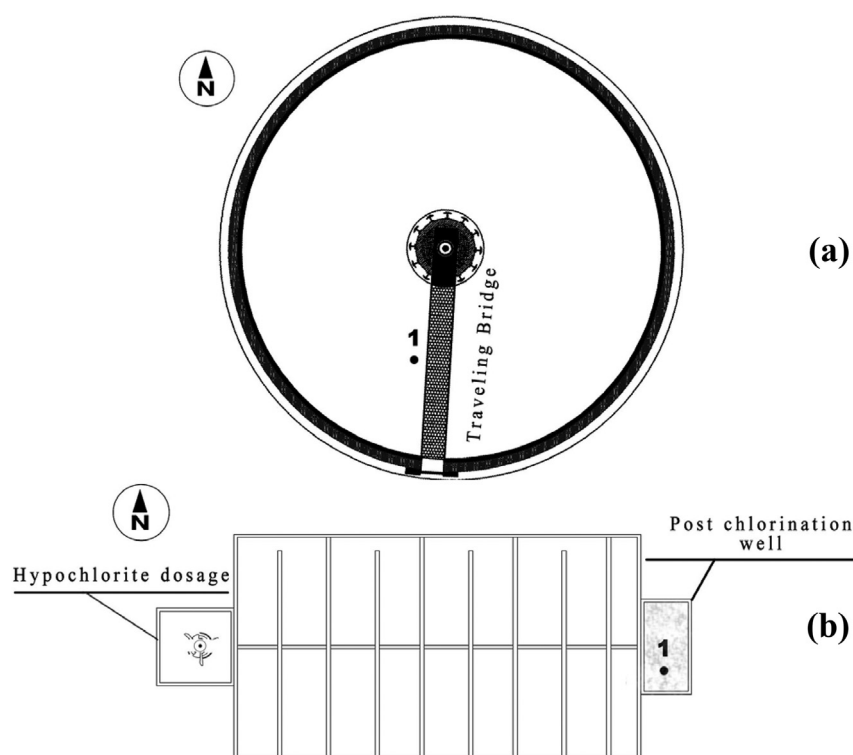| Sample	1	2	3	4	5	6	7	8	9	10	11	12
DO	5.96	5.53	5.28	5.43	6.10	5.95	5.37	5.61	5.4	5.89	4.47	4.97
T	18.66	18.45	18.52	18.43	18.47	18.48	18.75	18.52	18.55	18.49	18.48	18.77

Fig. 3. (a) Layout of the off gas sampling position in the secondary clarifier of the WWTP of Potenza. (b) Layout of the off gas sampling position in the disinfection unit of the WWTP of Potenza.

A comparison between the fluxes estimated via these two methods was done, in order to investigate the variation in determining the gas fluxes from non-aerated tanks by using different procedures.

2.5. Sampling procedure in chlorination

To our knowledge, the chlorination process has never been considered as a potential source of GHG in WRRFs. However, it could be a treatment unit considerably affecting the N_2O emissions. Indeed, NH_2OH is present in wastewater as an intermediate in nitrification processes (Ni et al., 2014; Pocquet et al., 2016) and its production is linked to an incomplete process due to unsuitable operational conditions. Thus, if NaClO is used as a disinfectant agent, the NH_2OH accumulated in the liquid phase during AS could be oxidized to N_2O in the disinfection unit.

Therefore, in order to collect an off-gas sample, the floating hood was positioned on the post-chlorination unit (Fig. 3b) where a considerable turbulence affected the stripping of dissolved N_2O (here called sN_2O), measuring an average flux of $1.04 \cdot 10^{-2}$ Nm^3 min^{-1}. The off gas leaving the liquid phase in the contact tank was neglected compared to the off-gas from the post-chlorination tank, due to very low turbulence and relatively low residence time in the contact tank.

2.6. Analytical methods

Analyses of COD, NH_4^+, NO_2^-, NO_3^- and TKN were carried out according to Standard Methods (APHA-AWWA-WEF, 2005). Mixed liquor suspended solids (MLSS) were measured by filtrating the activated sludge through 0.45 micro filter and then drying at 103–105 °C since constant weight. Volatile solids (MLVSS) were measured by heating the dried sample at 550 °C (APHA-AWWA-WEF, 2005).

Measurements of N_2O and CO_2 in gas and liquid phases were carried out by using a novel method, recently validated by Pascale et al., 2017, which includes a Shimadzu 2010 Plus Tracera gas chromatograph

(Kyoto, Japan), equipped with a 2 m × 1 mm (i.d.) ShinCarbon ST micropacked column (Restek, Bellefonte, USA) and a Barrier Ionization Discharge detector (BID). Experimental conditions were based on that reported by Pascale et al., 2017. In brief, the injection temperature was set to 150 °C. The oven temperature program was 30 °C (hold time for 5 min) and increased to 120 °C with a 10 °C min^{-1} rate. All injections were made in the direct mode. Helium was used as carrier gas at a flow rate of 15.0 ml min^{-1}. The BID detector was operated at 250 °C; 80 ml min^{-1} discharge gas flow was used for analysis. A 1 ml sample loop was employed for injection into GC-BID system. The pressure of the sample loop was fixed at $1.31 \cdot 10^5$ Pa (absolute pressure) for each injection. The greenhouse gas concentrations were quantified by comparing the peak areas of samples against the standard curves. The detection limits under these GC conditions were 62.04 μg l^{-1} and 5.26 mg l^{-1} for N_2O and CO_2, respectively. The relative standard deviations (RSD) of replicate standard measurements were 5.1% for N_2O and 6.6% for CO_2.

N_2O and CO_2 dissolved in liquid samples were extracted with the equilibration headspace technique (Kimochi et al., 1998): 65 ml of liquid sample, previously centrifuged at 4000 rpm for 5 min at room temperature, were transferred into a 120 ml glass vial (Sigma Aldrich, Milano, Italy). The vial was sealed with 20 mm PTFE/Silicone septa (Sigma Aldrich, Milano, Italy) with 55 ml headspace. After shaking, the vial was left at room temperature for 1 h without stirring. The resulting gas phase in head space was collected as a gas sample with a 60 ml syringe equipped with 3-way stopcocks valve. Then, the gas sample was injected in a 1 ml loop of the GC-BID system, similar to the gaseous samples.

The analytical method for the determination of dissolved NH_2OH in liquid samples, described by Seike et al. (2004), was applied and based on NH_2OH oxidation to N_2O using NaClO as the oxidizing agent, according to Eq. (4):

$$2NH_2OH + 2NaClO \rightarrow N_2O + 2NaCl + 3H_2O \qquad (5)$$

The produced N_2O was subsequently measured by using the headspace technique as described above. N_2O blank for each sample was measured without the addition of the NaClO solution in order to obtain the original amount of dissolved N_2O in the samples. NH_2OH was calculated as the difference between N_2O in the treated and untreated samples, respectively.

2.7. Estimation of N_2O emissions

The N_2O emission factor (EF) for all the monitored units was computed by normalizing the flux to the daily influent TKN, as reported by Chandran (2011). Thus, considering an average value of the influent NH_4^+ ($NH_4 - N_{in}$) from the data in Table 1 and the average flux ($\bar{Q}_{off-gas}$), the specific EF from the aerated compartment was calculated according to Eq. (6):

$$EF_{N2O} = \frac{\bar{N_2O}}{NH_4 - N_{in}} \cdot \bar{Q}_{off-gas} \qquad (6)$$

where $\bar{N_2O}$ is the weighted average value of the N_2O concentration on the recorded fluxes in each sampling point, calculated according to Eq. (2).

The $\bar{N_2O}$ flux was calculated as in Eq. (7):

$$N_2O\ flux = \frac{\bar{N_2O} \cdot \bar{Q}_{off-gas}}{A_{hood}} \qquad (7)$$

where $\bar{N_2O}$ is the weighted average concentration calculated as in Eq. (1), $\bar{Q}_{off-gas}$ is the average off-gas flow rate measured in AS (see Table 2), A_{hood} is the hood cross sectional area (i.e. 0.7 m^2).

3. Results and discussion

3.1. Concentration of dissolved N_2O ($\mu g\ l^{-1}$), NH_2OH ($\mu g\ l^{-1}$), and CO_2 ($mg\ l^{-1}$) along the water line

The obtained results are reported in Table 4. Three different samples were collected in the AS tank (points 1, 7 and 10 in Fig. 2) to monitor CO_2 and N_2O level profile along the unit length, and two samples were collected along the receiving water body in order to investigate the off-site effects of the residual dissolved gas. Indeed, the amount of residual gases in the liquid phase could be stripped in the receiving river, contributing to off-site emissions.

3.2. Estimation of N_2O emissions

According with Eq. (6), the value obtained for the specific EF from the aerated compartment is $3.39 \cdot 10^{-5}$ kg$_{N2O-N}$ kg$_{NH4-N}^{-1}$, corresponding to 0.0033%. The N_2O measured in this case study was relatively low. Even
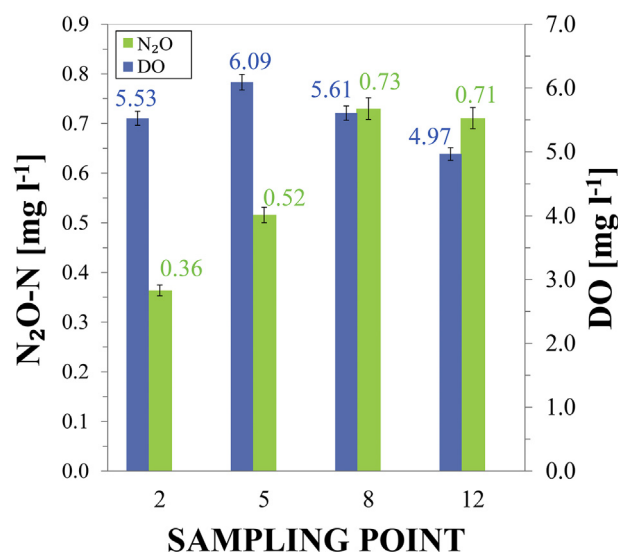
Fig. 4. A comparison between DO concentration (blue bar) and N_2O emissions (green bar) in AS.

if the IPCC (2006) established values to quantify the emissions, a reliable comparison is not possible because of the lack of a standard method for EF evaluations. Moreover, the GHG evaluation is characterized by a broad uncertainty due to plant configuration, operation parameters, seasonal conditions, and wastewater characterization, which is in contrast to the use of fixed EFs (Mannina et al., 2016; Gori et al., 2013).

In order to investigate the dependence of N_2O emissions from DO concentrations in AS, a comparison between DO and the emission values along the basin length was performed, with the choice of four sampling points along the basin length (points 2, 5, 8, 12 in Fig. 2). Fig. 4 shows the increase of N_2O emissions in correspondence with a DO concentration decrease, confirming other literature results (Kampschreur et al., 2009) and suggesting that N_2O emissions can be linked to the hydroxylamine oxidation pathway.

According with Eq. (7), an $\bar{N_2O}$ flux of 11.5 mg$_{N2O}$ min^{-1} m^{-2} was calculated.

Regarding the secondary settler, a linear regression was found in this study (Fig. 5 b) by using Eq. (3) and a gas flux ($N_2O\ flux$) of 0.48 mg$_{N2O}$ min^{-1} m^{-2} was estimated. Therefore, an EF of $1.42 \cdot 10^{-6}$ kg$_{N2O-N}$ kg$_{NH4-N}^{-1}$ was calculated, corresponding to $1.4 \cdot 10^{-4}$%, in accordance to Eq. (7), where $NH_4 - N_{in}$ is the amount of ammonia nitrogen as N in the influent wastewater:

$$EF_{N2O,settler} = \frac{N_2O\ flux}{NH_4 - N_{in}} \qquad (8)$$

Table 4
Concentration of dissolved N_2O (sN_2O in $\mu g\ l^{-1}$), NH_2OH ($\mu g\ l^{-1}$), CO_2 ($mg\ l^{-1}$), NH_4^+ ($mg\ l^{-1}$), N-NO$_2^-$ ($mg\ l^{-1}$) and N-NO$_3^-$ ($mg\ l^{-1}$) along water line. Each concentration value was averaged of three replicates (independent samples) and the error was within 5%.

|	sN_2O ($\mu g\ l^{-1}$)	NH_2OH (as N_2O) ($\mu g\ l^{-1}$)	sCO_2 ($mg\ l^{-1}$)	NH_4^+ ($mg\ l^{-1}$)	N-NO$_2^-$ ($mg\ l^{-1}$)	N-NO$_3^-$ ($mg\ l^{-1}$)
Incoming wastewater	–	–	938.21	9.61	–	0.1300
AS_influent	–	–	–	2.48	–	0.7540
AS_point 1 (1 in Fig. 2)	126.91	207.02	2728.57	0.638	0.181	12.7
AS_point 2 (7 in Fig. 2)	130.55	214.17	3298.92	1.3	0.958	19.4
AS_point 3 (10 in Fig. 2)	140.12	217.68	3756.73	0.702	0.336	13.6
AS effluent	137.82	216.59	3974.65	1.93	0.338	17.5
Secondary settler	131.36	213.65	2815.75	–	–	–
Clarifier effluent	130.55	212.61	2803.66	0.035	–	4.91
Chlorination effluent	346.90	1.04	2078.53	–	–	–
Post-chlorination well	133.3	1.66	1223.04	–	–	–
Final effluent	9.09	–	1351.92	0.25	–	8.34
River water	195.09	127.09	925.80	–	–	–
River water post-exhaust	197.74	122.59	1252.38	–	0.074	3.15
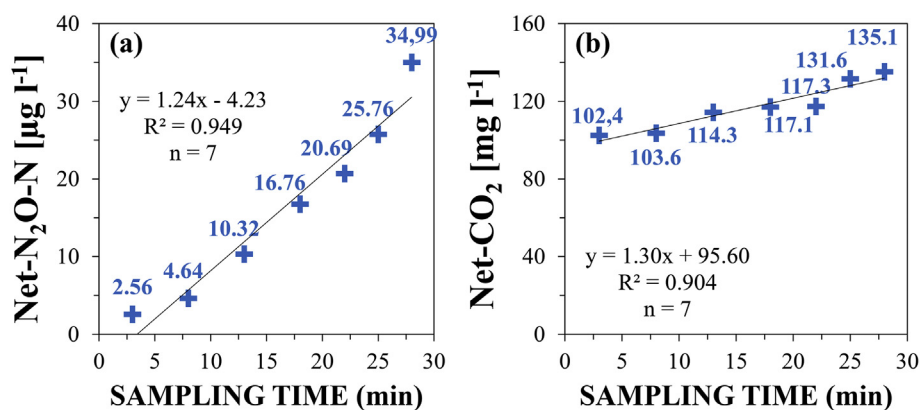
Fig. 5. (a) Linear regression of N_2O concentration versus sampling time. (b) Linear regression of CO_2 concentration versus sampling time.

The gas flux calculated via the method proposed by Chandran (2011) (Eq. (4)) was 0.0083 mg_{N2O} min^{-1} m^{-2}, corresponding to 2.45 · 10^{-6}% as EF according to Eq. (6).

In Fig. 5, it is evident that N_2O and CO_2 emissions are very different. The net CO_2 production is due mainly to the higher occurrence of carbonaceous compounds compared to nitrogenous mass and their faster biodegradation in the previous aerated unit. Moreover, this result also could be explained considering that in a passive surface, such as secondary clarifier, the mass transfer is mainly related to the gas solubility: being CO_2 more soluble, its interface concentration should be higher than N_2O's one.

As expected, the emissions from the secondary clarifier were smaller than those from the aerated compartments mainly because of low off-gas flow rates due to the absence of an aeration system, providing a very low stripping effect.

The scientific literature values are in the range of 0.00248–0.66 mg_{N2O} min^{-1} m^{-2}. In particular, a range of 0.00248–0.065 mg_{N2O} min^{-1} m^{-2} is established for physical separation units (i.e. settlers and thickeners) (Uggetti et al., 2012; Chandran, 2011). In this study, the obtained results of GHG measured fluxes show that the Chandran method, usually used in the literature, underestimates the emission fluxes. This comparison confirms the need to develop and validate a standard method to measure N_2O and CO_2 emission from non-aerated tanks.

Regarding the disinfection unit, interesting results were found confirming that the chlorination unit is the major contributor to N_2O emissions in this study, estimating an EF value of 0.00022 kg_{N2O-N} kg_{NH4-N}^{-1} or 0.022%, according to Eq. (6).

The NH_2OH produced during the nitrification processes in the previous biological compartment reaches the disinfection unit as a dissolved compound. Then, the chemical reaction with the disinfecting agent (i.e., NaClO) favors its transformation into N_2O, which is then emitted in the post-chlorination well where the stripping is promoted, due to the presence of turbulence. This result is one of the key novelties of this study, which suggests that more data are needed to characterize chlorination unit as a potential source of N_2O in WRRFs.

The N_2O flux from chlorination unit was also calculated as suggested in Eq. (7), using the N_2O concentration measured in the post-chlorination well as $\overline{N_2O}$, and the flow meter result as $\overline{Q}_{off-gas}$. A value of 11.1 mg_{N2O} min^{-1} m^{-2} was recorded.

Fig. 6a and b shows a comparison among the trends of nitrogen species (NH_4^+, NO_2^--N, NO_3^--N, N_2O, NH_2OH), in wastewater and off-gas, in order to investigate the fate of N_2O after wastewater treatment and to carry out interesting considerations about the chlorination unit. Particularly, the comparison between Fig. 6a and b shows that part of the NH_2OH dissolved in the clarifier effluent is transformed into N_2O in the chlorination unit, where the N_2O concentration in the liquid phase

increased from 0.131 mg l^{-1}, in the influent to the chlorination tank, to 0.347 mg l^{-1} in its effluent. This result confirms the chemical interaction between NH_2OH and NaClO, strengthening the hypothesis that the
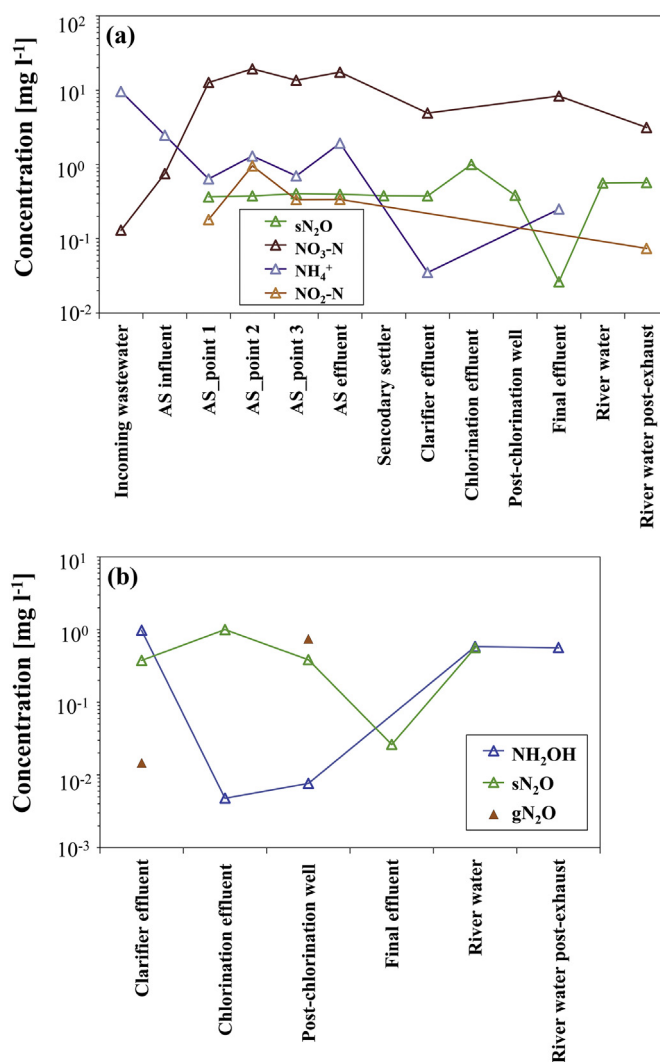

Fig. 6. (a) Comparison between N_2O and nitrogen species in the liquid phase. sN_2O was assumed negligible, and not measured, in the influent of the WRRF. (b) Comparison of N_2O liquid and gas, and NH_2OH. gN_2O was not measured in the chlorination unit, the final effluent and the river water.

chlorination unit can be a weighty contributor in the net CFP calculation. Moreover, an increase of both N_2O and NH_2OH loads in the final effluent was found, thus proving that BNR processes probably occur in the river by involving the residual nitrogen compounds and thus contributing to the off-site direct GHG emissions.

Further comparison between Fig. 6a and b highlights the relationship between the NH_4^+ load and the N_2O emissions during wastewater treatment: the decrease in NH_4^+ load (blue line in Fig. 6a) and the enhancement of NO_3^--N (brown trace in Fig. 6a) attests to the occurrence of nitrification processes in AS, which consequently promotes the N_2O formation in the liquid phase (green line in Fig. 6b). This correlation, combined with the high DO concentration confirms the hypothesis that N_2O emissions can be linked to the hydroxylamine oxidation pathway (Law et al., 2012; Vasilaki et al., 2018). In AS, the stripping of N_2O occurs due to the presence of aeration devices (the aeration affects the steps occurring from AS influent to AS effluent in Fig. 6), thus a considerable concentration of N_2O in the off-gas (orange triangles in Fig. 6b, called gN_2O) is observed. In the clarification tank (from AS effluent to clarifier effluent in Fig. 6), nitrification processes probably occur because a decrease in NH_4^+ concentration is found and the residual concentration of sN_2O in the wastewater is slowly stripped here.

During chlorination (from clarifier effluent to final effluent in Fig. 6) the considerable increase of sN_2O due to the chemical reaction between NH_2OH and $NaClO$ was followed by an abrupt decrease because of turbulence in the post-chlorination well, favoring N_2O stripping.

3.3. Estimation of on-site direct emissions

Assuming a conversion factor of 0.74 kg_{bCOD} kg_{COD}^{-1} (Henze et al., 2000), the specific amount of equivalent CO_2 ($CO_{2,eq}$) emitted from AS, secondary clarifier, and chlorination due to the direct transformation of biodegradable organic matter and nutrients was also calculated, as mass of $CO_{2,eq}$ per mass of influent biodegradable COD (bCOD).

According to Eqs. (9) and (10), average CO_2 and N_2O emission fractions for AS were 0.068 kg_{CO2} kg_{bCOD}^{-1} and 0.00112 $kg_{CO2,eq}$ kg_{bCOD}^{-1}, respectively, calculated by weighing the local loads at each sampling point by the relative fluxes and using the N_2O global warming potential of 289 $kg_{CO2,eq}$ kg_{N2O}^{-1} (IPCC, 2006):

$$EF_{AS,CO2} = \frac{\overline{CO_2}}{bCOD_{in}} \cdot \bar{Q}_{off-gas} \qquad (9)$$

$$EF_{AS,N2O} = \frac{\overline{N_2O}}{bCOD_{in}} \cdot \bar{Q}_{off-gas} \cdot 289 \qquad (10)$$

where $\overline{N_2O}$ and $\overline{CO_2}$ are the weighted average concentrations of N_2O and CO_2 in the off-gas, respectively, calculated according to Eqs. (1) and (2), $\bar{Q}_{off-gas}$ is the average off-gas flow rate measured in AS, and $bCOD_{in}$ is the influent biodegradable COD calculated as the mean value of the data in Table 1.

A value of 200,388 mg_{CO2} min^{-1} m^{-2} was found as $\overline{CO_2}$ flux, calculated as in Eq. (11):

$$CO_2 flux = \frac{\overline{CO_2} \cdot \bar{Q}_{off-gas}}{A_{hood}} \qquad (11)$$

where $\overline{CO_2}$ is the weighted average concentration calculated as in Eq. (2), $\bar{Q}_{off-gas}$ is the average off-gas flow rate measured in AS (see Table 2), A_{hood} is the hood cross sectional area.

Regarding the secondary settler, the CO_2 produced from the biodegradation of organic matter was analysed via the Uggetti method (Eq. (3)). The linear regression of CO_2 concentration versus sampling time (Fig. 5b) gives a gas flux (CO_2 flux) of 520 mg_{CO2} min^{-1} m^{-2}.

An EF of $1.7 \cdot 10^{-4}$ kg_{CO2} kg_{bCOD}^{-1} was calculated (Eq. (12)) considering the CO_2 emissions due to biodegradation processes, where $bCOD_{in}$ is the influent biodegradable COD calculated as the mean value of the data in Table 1:

$$EF_{CO2,settler} = \frac{CO_2 \, flux}{bCOD_{in}} \qquad (12)$$

The gas flux calculated via the Chandran method (Eq. (4)) was 55.86-mg_{CO2} min^{-1} m^{-2}. Therefore, an EF of $1.89 \cdot 10^{-5}$ kg_{CO2} kg_{bCOD}^{-1} was calculated. The results obtained using the two proposed methods (Uggetti et al., 2012 and Chandran, 2011) differ by an order of magnitude, and confirm the underestimation of the Chandran method. The chlorination unit can be considered the major contributor to N_2O emissions, which accounts for the global warming potential of N_2O and translates into 0.008 $kg_{CO2,eq}$ kg_{bCOD}^{-1}. In Table 5 a comparison among the direct onsite emissions, as well as the CO_2 and N_2O fluxes, from each investigated treatment unit is reported.

The results show that the aeration tank and the chlorination unit are the major contributors to CO_2 and N_2O emissions, respectively. In particular, the N_2O fluxes from these treatment units are comparable and equal to c.a. 11 mg_{N2O} min^{-1} m^{-2}. Therefore, even though the chlorination process is not a biological treatment step, its N_2O emissions could not be neglected because the fluxes were of the same order as those of the AS tank. These findings confirm our expectations when considering the disinfection using $NaClO$ as a N_2O potential source. Regarding the secondary settler, the fluxes of both CO_2 and N_2O are negligible in comparison with those from AS and chlorination, justifying the lowest direct emissions.

3.4. Estimation of eFP and on-site indirect emissions

Energy demand for the main wastewater treatments was initially evaluated by taking into account the average influent COD value (Table 1).

Table 6 shows the specific working power, and thus the specific energy consumption, of the main mechanical systems involved in the WRRF function which work continuously for 24 h per day:

Assuming a conversion factor of 0.74 kg_{bCOD} kg_{COD}^{-1} (Henze et al., 2000), the net eFP for the AS configuration was 1.93 kWh kg_{bCOD}^{-1} which also accounts for the denitrification and oxidation compartments,

Table 5
Comparison among the obtained results about direct on-site emissions from each investigated unit.

Treatment units	Direct on site emissions $kg_{CO2,eq}$ kg_{bCOD}^{-1}		N_2O emission factor kg_{N2O-N} kg_{NH4-N}^{-1}	Gas fluxes mg min^{-1} m^{-2}	
	CO_2	N_2O		CO_2	N_2O
Aeration tank	0.068	0.00112	$3.39 \cdot 10^{-5}$	200,388	11.5
Secondary settler	0.00017	$4.71 \cdot 10^{-5}$	$1.42 \cdot 10^{-6}$ (Uggetti method)	520 (Uggetti method)	0.48 (Uggetti method)
			$2.45 \cdot 10^{-8}$ (Chandran method)	55.86 (Chandran method)	0.0083 (Chandran method)
Chlorination unit	–	0.008	0.00022	–	11.1

Table 6
Energy consumption of the main mechanic systems.

Treatment units	Mechanic system	No. of working units	Power [kW]	Energy consumption [kWh day^{-1}]
AS compartment	Mixer	3	11	792
	Submerged air pump	3	15	1080
	Blower	2	132	6336
	Net energy consumption in AS			8208
Settler	Bridge	2	3	144
Chlorination unit	Mixer	1	4	96
	Dosing pump	1	0.24	5.76
	Net energy consumption in chlorination			101.76

according to Eq. (13):

$$eFP = \frac{Net\ energy\ consumption\ \left[\text{kWh day}^{-1}\right]}{bCOD_{in}\ \left[\text{kg day}^{-1}\right]} \tag{13}$$

Therefore, the corresponding production of on-site indirect $CO_{2,eq}$ emissions, related to on-site electricity consumption, was 0.786 kg$_{CO2,eq}$ kg$_{bCOD}^{-1}$, when considering an emission factor of 0.406 kg $CO_{2,eq}$ kWh^{-1} as a typical value for Italian WRRFs (IEA, 2012).

Particularly, two blowers working at the rate of 132 kW for 24 h were used to transfer oxygen in AS and the specific eFP for the aeration was 1.49 kWh kg$_{bCOD}^{-1}$ (calculated according to Eq. (11)), which corresponds to 0.606 kg$_{CO2,eq}$ kg$_{bCOD}^{-1}$ as on-site indirect $CO_{2,eq}$.

The value obtained in this study is consistent with available scientific literature and lies within the main variability range of 0.6–0.7 kg$_{CO2,eq}$ kg$_{bCOD}^{-1}$.

Two traveling bridges working at the rate of 3 kW for 24 h were used in the clarifier step and the specific eFP was 0.034 kWh kg$_{bCOD}^{-1}$, which corresponds to the production of on-site indirect $CO_{2,eq}$ emissions equal to 0.014 kg$_{CO2,eq}$ kg$_{bCOD}^{-1}$. The eFP for the chlorination unit was evaluated considering the mixer and dosing pump for the NaClO supply. The specific energy demand was 0.023 kWh kg$_{bCOD}^{-1}$, which corresponds to 0.01 kg$_{CO2,eq}$ kg$_{bCOD}^{-1}$ as on-site indirect emissions.

As expected, the aeration system is the main contributor to total site wide indirect emissions and covers 96.3% of the monitored units.

The comparison between direct and indirect emissions is reported in Table 7.

4. Conclusions

In this study, the energy and carbon footprints of a medium sized wastewater treatment plant were evaluated to support the development of innovative tools to monitor GHG emissions, as well as promote control strategies to improve plant performance, thus ensuring higher water quality, sustainable costs, and minimized environmental impacts.

The off-gas technique allowed the evaluation of both CO_2 and N_2O emissions from treatment units and receiving water body, even though more attention was given to N_2O due to its larger global warming potential. The quantity and distribution of produced GHG depends on wastewater characteristics and operational parameters, thus

Table 7
Comparison between on-site direct emissions and indirect emissions.

Treatment units	Direct on site emissions kg$_{CO2,eq}$ kg$_{bCOD}^{-1}$		Indirect emissions kg$_{CO2,eq}$ kg$_{bCOD}^{-1}$
	CO_2	N_2O	CO_2
Aeration tank	0.068	0.00112	0.786
Secondary settler	0.00017	$4.71 \cdot 10^{-5}$	0.014
Chlorination unit	–	0.008	0.010

correlations with measured concentration, e.g. DO, NH_4, NH_2OH, were carried out. The most important innovative aspects of the study are represented by the evaluation of the emissions as related to the chlorination unit and to the secondary clarifier. Indeed, for the first time, we applied and compared two different methods (the Uggetti et al., 2012 method and the Chandran, 2011, method) for the measurement of GHG emissions from non-aerated tanks and found that the Chandran methods provides lower emission factors compared to the Uggetti method, which was applied for the first time in non-aerated water tank. The results show that further investigation is needed in order to standardize and validate a reliable method for the measurement of GHG emissions from non-aerated tanks.

Furthermore, a first attempt to measure N_2O emissions from the chlorination unit is reported. The off-gas testing performed during the monitoring campaign proved that the chlorination unit is the major contributor to N_2O emissions due to the chemical reaction between NH_2OH and disinfectant agent (i.e. NaClO), showing that its contribution to emissions may not be negligible. In terms of $CO_{2,eq}$ related to the biodegradation of organic matter and nutrients, the AS tank mainly contributes to emissions. The energy footprint calculation confirms that the aeration system is the largest contributor to $CO_{2,eq}$ emissions from imported power.

Conflict of interest

The authors have no conflict of interest to declare.

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